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Thermodynamic Properties of Certain Acetylenic Peroxy Derivatives of *o*- and *m*-Carboranes

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Abstract—Temperature dependences of heat capacity of seven peroxy-containing *o*- and *m*-carborane derivatives were determined for the first time. The entropies and Gibbs energies of formation of these compounds were calculated. The enthalpies, entropies, and Gibbs energies of *meta–para* transitions were determined for two pairs of isomers in the condensed and gas phases.

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Peroxy derivatives of 12-carboranes hold promise for application, since their introduction in polymeric chains strongly enhances resistance of the latter to thermooxidative destruction and UV and γ irradiation [1–3]. We previously reported the enthalpies of formation of six carboranes [4, 5] and the vaporization enthalpies of seven carboranes [6].

The present work reports for the first time experimental temperature dependences of heat capacity for the following seven peroxy carboranes: 3-[*m*- and *o*-(carboranylcarbonyl)peroxy]-3-methylbut-1-yne (**I**, **II**) (cr.), 3-[(2-isopropyl-*m*-(carboranylcarbonyl)peroxy)]-3-methylbut-1-yne (**III**) (l.), 3-[(7-isopropyl-*o*-(carboranylcarbonyl)peroxy)]-3-methylbut-1-yne (**IV**) (cr.), 2-(*tert*-butylperoxy)-2,5-dimethyl-5-[*m*-(carboranylcarbonyl)peroxy)]hex-3-yne (**V**) (l.), 2,5-bis[*m*-(carboranylcarbonyl)peroxy)]-2,5-dimethylhex-3-yne (**VI**) (cr.), and bis(2,2-dimethylprop-2-yn-1-yl) *m*-carborane-1,7-dicarbodiperoxoate (**VII**) (cr.).

$HC{\equiv}CC(CH_3)_2OOC(O)CB_{10}H_{10}CH$
m-**I**, *o*-**II**

$HC{\equiv}CC(CH_3)_2OOC(O)CB_{10}H_{10}CCH(CH_3)_2$
m-**III**, *o*-**IV**

$(CH_3)_3COOC(CH_3)_2C{\equiv}CC(CH_3)_2OOC(O)CB_{10}H_{10}CH$
m-**V**

$HCB_{10}H_{10}CC(O)OOC(CH_3)_2C{\equiv}CC(CH_3)_2OOC(O)CB_{10}H_{10}CH$
m-**VI**

$HC{\equiv}C(CH_3)_2COO(O)CCB_{10}H_{10}CC(O)OOC(CH_3)_2C{\equiv}CH$
m-**VII**

The resulting data allowed calculation of the entropies and, together with the enthalpies of formation reported in [4, 5] and obtained in the present work for compound **III**, Gibbs energies of formation of these compounds.

To calculate the standard enthalpies of formation at 298.15 K, one should integrate the temperature dependence of C_p in the range 0–298.15 K. The primary data for the temperature dependence of C_p in the range 180–320 K are given in Table 1.

The $C_p = f(T)$ dependences below 180 K are impossible to measure on a Perkin–Elmer DSC-1B calorimeter. The $C_p = f(T)$ dependences in the range 0–298.15 K were obtained by extrapolation of the dependences in the range 180–320 K to absolute zero temperature on the assumption that $C_p(T{=}0) = 0$. Evidence for the validity of this approach comes from the results of Diot et al. [7] on the heat capacities of $\{(C_2H_5)_4N\}_2B_{10}H_{10}$ and $\{(C_2H_5)_4N\}_2B_{12}H_{12}$ at low temperatures (0–150 K), who showed that the heat capacity curves at 0–150 K show no anomalous deviations caused by changes in carborane skeleton motion (internal and external), as well as changes in molecular motion in whole.

The resulting $C_p = f(T)$ dependences were fitted by Eq. (1). The equation for the standard entropy of condensed compounds at 298.15 K ($S^0_{298.15}$) takes form (2).

$$C_p = a + bT + cT_2 + dT_3 + fT_4, \qquad (1)$$

$$S^0_{298.15} = \int_0^{298.15} \frac{C_p}{T}\, dT\,. \qquad (2)$$

The error in the calculated standard absolute entropy corresponds to the error in calculation of in-

Table 1. Temperature dependence of heat capacity for compounds **I–VII**, $\mathrm{J\,mol^{-1}\,deg^{-1}}$

T, K	**I**	**II**	**IV**	**VI**	T, K	**III**	**V**	**VII**
190	190.5	143.9	246.5	481.0	185	343.1	367.9	375.0
200	208.9	160.4	297.9	517.5	195	377.7	396.1	413.8
210	227.4	176.9	289.2	552.6	205	418.0	421.9	455.9
220	245.9	193.4	310.7	585.9	215	426.6	445.2	499.1
230	264.4	209.9	332.0	617.1	225	509.8	466.1	541.3
240	282.9	226.5	353.5	646.3	235	556.6	484.6	581.4
250	301.3	242.9	374.9	671.5	245	602.7	500.9	619.7
260	319.9	259.4	396.3	698.7	255	647.1	515.2	656.2
270	338.4	276.0	417.6	724.8	265	692.8	526.9	691.2
280	356.8	292.4	439.1	749.8	275	735.6	540.2	724.6
290	375.4	309.0	460.5	769.2	285	775.4	552.1	749.6
300	393.8	325.5	481.7	790.7	295	810.4	564.4	776.1
310	412.3	342.0	503.2	811.2	305	839.6	577.5	799.8
320	430.8	358.4	524.6	830.8	315	862.7	591.6	830.5

Table 2. Coefficients of the $C_p = f(T)$ dependences and entropies of carboranes **I–VII**

Comp. no.	S_n	Coefficients of Eq. (1)					$S^0_{298.15}$, $\mathrm{J\,mol^{-1}\,deg^{-1}}$	$-\Delta_f S^0_{298.15}$, $\mathrm{J\,mol^{-1}\,deg^{-1}}$
		$a \times 10^2$	$b \times 10$	$c \times 10^3$	$d \times 10^5$	$f \times 10^7$		
I	0.962	1.868	–1.919	8.375	–1.112	–	216.7 ± 4.6	1370.9 ± 4.6
II	2.688	2.986	–0.3012	4.753	–0.3637	–	170.1 ± 9.6	1417.5 ± 9.6
III	1.180	4.893	34.58	–41.0	24.78	–3.964	642 ± 18	1355 ± 18
IV	3.705	13.98	–3.728	12.19	1.765	–	275 ± 16	1721 ± 16
V	4.401	–20.26	11.34	8.494	1.968	–	541 ± 19	2207 ± 19
VI	2.526	–10.31	7.761	14.81	2.860	–	636 ± 20	2397 ± 20
VII	4.552	64.83	13.340	–8.305	10.37	–2.050	543 ± 17	1778 ± 17

tegral (2), including the errors in measurement of the $C_p = f(T)$ dependence and temperature, as well as in interpolation of the $C_p = f(T)$ dependence in the low-temperature range [8]. The coefficients a, b, c, d, and f of the resulting dependences, the rms deviations of the polynomials of the experimental points (S_n), and the calculated entropies are listed in Table 2. The entropies of formation $\Delta_f S^0_{298.15}$ of the compounds (Table 2) were calculated with the following $S^0_{298.15}$ values, $\mathrm{J\,mol^{-1}\,deg^{-1}}$: C(graphite) 5.74, B(cr.) 5.87, H_2(gas) 130.6, O_2(gas) 205.03 [9].

The combustion reaction of compound **III** is given by Eq. (3):

$$C_{11}B_{10}H_{24}O_{3(l.)} + 23O_{2(gas)} + 3H_2O_{(l.)}$$
$$11CO_{2(gas)} + 10H_3BO_{3(cr.)}. \qquad (3)$$

The liberated boric acid deposited mostly on the wire gauze, electrodes, and bomb walls as a fine white powder. Before experiment the bomb was charged with 1 ml of water a part of which was spent, according to Eq. (3), for formation of boric acid and the rest dissolved a certain (to saturation) quantity of the latter. After burning, the bomb contained, along with the products shown in Eq. (3), ca. 1 ml of saturated aqueous H_3BO_3 and minor quantities of boron, carbon, and boron carbide.

The energy of combustion was calculated by Eq. (4).

$$-U^0_{298.15} = 1/m_s[q_{tot} - q_{Ter} - q_{mar} - q(HNO_3)$$
$$+ q(H_3BO_3) + q_B + q_C - \Delta U_W). \qquad (4)$$

Here m_s is the sample weight; q_{tot} is total heat evolved; q_{Ter}, q_{mar} are correction for the combustion of auxiliary substances (Terylene capsule and gauze); $q(HNO_3)$ is a correction for formation of dilute HNO_3; $q(H_3BO_3)$ is a correction for partial dissolution of

Table 3. Experimental determination of the heat of combustion of 3-[(2-isopropyl-*m*-(carboranylcarbonyl)peroxy)]-3-methylbut-1-yne (**III**)

m_c, g	Combustion products, %		q_{tot}, J	$q(HNO_3)$, J	q_{Ter}, J	q_{thread}, J	q_B, J	q_C, J	$q(H_3BO_3)$, J	$-\Delta U_i^0$, J g^{-1}
	B	C								
0.09146	0.9700	0.9710	5398.7	3.0	1231.3	138.9	56.7	36.8	16.0	45077
0.07173	0.9784	0.9824	4496.4	2.8	1205.1	139.3	32.0	17.5	16.1	44733
0.07013	0.9750	0.9747	4532.7	2.1	1324.2	125.7	36.2	24.6	16.1	44980
0.10132	0.9680	0.9767	6049.3	4.0	1468.8	140.0	66.9	32.7	16.0	44896
0.09320	0.9811	0.9798	5724.4	3.1	1506.2	124.2	36.4	26.1	16.0	44698
0.13201	0.9443	0.9514	7484.2	2.2	1495.1	142.0	151.8	88.9	15.9	46196
0.08228	0.9552	0.9655	5224.0	2.7	1437.3	163.2	76.1	39.3	16.0	45564

H_3BO_3; q_B and q_C are corrections for incomplete combustion with respect to boron and carbon; ΔU_W is a correction on reduction of the initial and final states of compounds in the calorimetric bomb to the standard state (Washburn correction).

In the calculation we used the following heats of combustion (J g^{-1}) in a bomb: Terylene 22944.2 [10], gauze and thread –16704.2 [11], boron to $H_3BO_{3(cr.)}$ –61379 [12], carbon to $CO_{2(gas)}$ –92763 [13], formation of HNO_3 59 kJ mol^{-1} [14], and formation of a saturated solution of H_3BO_3 –21836 kJ mol^{-1} [14].

Analysis of the resulting data revealed certain correlations between the combustion efficiency in separate experiments (ΔU_i) and combustion efficiency with respect to carbon (C). These correlations can be explained by the formation of boron carbide whose quantity is practically impossible to determine. When the combustion efficiency of the carborane-containing compounds is higher than 99%, the correction for the heat of formation of boron carbide is reasonably neglected [12]. If this correction is neglected at lower combustion efficiencies, the quantities of the free boron and carbon formed by combustion are overestimated, which results in overestimated heats of combustion. The fitting of the dependences of the combustion energies of peroxides on their combustion incompleteness with respect to carbon (100 – C) by Eq. (5) gave fair results (correlation coefficient ρ 0.9806).

$$\Delta U = a + b(100 - C). \qquad (5)$$

The a term in Eq. (5) is the energy of complete (100%) combustion with respect to carbon (ΔU_{100}). The coefficients of the straight-line equation were obtained by the least-squares method. The resulting data for compound **III** are given in Table 3. The combustion efficiency with respect to boron is labeled B.

The Washburn correction calculated according to [13, 15] was 3.2 J g^{-1}. The standard enthalpy of combustion $\Delta_c H^0_{298.15}$ was calculated from the standard combustion heat ΔU^0_{100} and the expansion work ΔnRT by Eq. (6).

$$\Delta_c H^0_{298.15} = \Delta U^0_{100} + \Delta nRT. \qquad (6)$$

Here Δn is the difference in the number of gas moles before and after combustion. The standard enthalpies of formation $\Delta_f H^0_{298.15}$ of peroxides were calculated from the resulting $\Delta_c H^0_{298.15}$ values and the standard enthalpies of formation of the components of the combustion reaction (kJ mol^{-1}): $H_3BO_{3(cr.)}$ 1094.99 ± 1.3 [13], $CO_{2(gas)}$ 398.512 ± 0.046, $H_2O_{(l.)}$ 285.829 ± 0.040 [8]. The $\Delta_f H^0_{298.15}$ values for compound **III** and those for compounds **I**, **II**, and **IV**–**VII** from [4, 5] are given in Table 4.

The standard Gibbs energies of formation of the compounds in the condensed state at 298.15 K were calculated by Eq. (7) and the standard entropies of vaporization ($\Delta_{sub(vap)}S^0$), by Eq. (8).

$$\Delta G^0_{298.15} = \Delta_f H^0_{298.15} - 298.15\Delta_f S^0_{298.15}, \qquad (7)$$

$$\Delta_{sub(vap)}S^0_T = \Delta_{sub(vap)}H_T/T + R\ln P/P_0. \qquad (8)$$

Here $\Delta_{sub(vap)}H_T$ are the equilibrium enthalpies of vaporization of the compounds [6] and P and P_0, saturated vapor pressures of the condensed phase at temperature T and normal boiling point, respectively.

The absolute entropies $-\Delta S^0_{gas}$ in the gas phase were calculated by Eq. (9) and the standard Gibbs energies of formation in the gas phase, by Eq. (10).

$$S^0_{gas} = S^0_{cond} + \Delta_{sub(vap)}S^0, \qquad (9)$$

$$\Delta_f G^0_{298.15,\,gas} = \Delta_f G^0_{298.15,\,cond} - RT\ln P/P_0. \qquad (10)$$

Table 4. Thermodynamic properties of compounds **I–VII**

Comp. no.	$-\Delta_f H^0_{298.15,\,\mathrm{cond}}$, kJ mol^{-1}	$\Delta_f H^0_{298.15,\,\mathrm{cond}}$, kJ mol^{-1}	$\Delta_{\mathrm{sub(vap)}} H_T$, kJ mol^{-1} [6]	$\Delta_{\mathrm{sub(vap)}} S^0_T$, J mol^{-1} deg^{-1}	$S^0_{298.15,\,\mathrm{gas}}$, J mol^{-1} deg^{-1}	$\Delta_f G^0_{298.15,\,\mathrm{gas}}$, kJ mol^{-1}
I	382 ± 14	27 ± 14	109.6 ± 3.2	230.8 ± 9.8	448 ± 11	68 ± 14
II	316 ± 16	107 ± 16	113.1 ± 2.4	243.9 ± 7.5	414 ± 12	147 ± 16
III	719 ± 26	–315 ± 26	93.0 ± 2.4	179.5 ± 6.9	822 ± 19	–275 ± 26
IV	639 ± 23	–126 ± 23	122.1 ± 1.9	256.5 ± 5.4	532 ± 17	–80 ± 23
V	675.3 ± 9.2	–17.4 ± 9.2	–	–	–	–
VI	706 ± 28	9 ± 28	–	–	–	–
VII	713 ± 26	–183 ± 26	–	–	–	–

Table 5. Thermodynamic parameters of *ortho–meta* transition

Isomerization	$\Delta_{o\to m} H^0_{298.15\,\mathrm{K}}$, kJ mol^{-1}		$\Delta_{o\to m} S^0_{298.15\,\mathrm{K}}$, J mol^{-1} geg^{-1}		$\Delta_{o\to m} G^0_{298.15\,\mathrm{K}}$, kJ mol^{-1}	
II → I	Crystal → crystal	Gas → gas	Crystal → crystal	Gas → gas	Crystal → crystal	Gas → gas
	–66 ± 21	–68 ± 21	+47 ± 11	+34 ± 16	–80 ± 21	–79 ± 21
IV → III	Crystal → liquid	Gas → gas	Crystal → liquid	Gas → gas	Crystal → liquid	Gas → gas
	–80 ± 34	–109 ± 34	+367 ± 24	+290 ± 25	–189 ± 34	–195 ± 34

The calculated values are listed in Table 4. They were used to calculate the enthalpies, entropies, and Gibbs energies of *ortho–meta* transitions for the isomer pairs studied in the condensed and gas phases (Table 5). For both isomer pairs, the enthalpies and Gibbs energies of the *ortho–meta* transition are negative values, while the entropies are positive. This fact suggests that the *meta* isomers are thermodynamically more stable and stronger disordered.

EXPERIMENTAL

The procedures for synthesis of the compounds studied are given in [16, 17]. Crystalline compounds were purified by low-temperature crystallization, and liquid compounds, by column chromatography. The composition of the compounds were determined by the elemental analyses, molecular weights, active oxygen contents, and IR spectra. The purity of the compounds was confirmed by TLC on Silufol UV-254.

The temperature dependences of heat capacity were measured on a Perkin–Elmer DSC-1B differential scanning calorimeter with an EMU universal gauge and a special computer software. The measurements were performed in the range 180–320 K using liquid nitrogen. The temperature scan rate was 4 deg min^{-1}. Mean cell temperature rise per one signal 10 deg, signal time 2–3 min. The cell system was continuously purged with nitrogen. Sample weight ca. 10 mg, weighing accuracy $\pm 1 \times 10^{-6}$ g.

The heat of combustion of compound **III** was measured on a B-06-μ combustion calorimeter. The energy equivalent of the calorimetric system (W 13322 ± 4 J V^{-1}) was determined using K-1 benzoic acid as reference (standard combustion energy ΔU_B –26434.4 J g^{-1}).

Before combustion the samples were sealed in capsules of Terylene film. The main problem in working with such compounds was that if the capsule is sealed insufficiently tightly part of the substance vaporizes and remains uncombusted during experiment or combusted in the gas phase. To go around this problem, two-necked Terylene capsules were used: a narrower internal and a wider external. After loading the internal capsule, the external was sealed with hot air. Thus prepared container was wrapped with a gauze strip ca. 125 mm, through which cotton thread was run. The container was then mounted on a platinum gauze attached to a platinum-screened dish holder. The thread was ignited with a capacitor discharge through a platinum wire 0.1 mm in diameter. The gauze strip provided uniform flame propagation over the sample surface. The electrodes, too, were screened with platinum for complete sample combustion. The oxygen pressure in the bomb was 3.0×10^6 Pa. Under the above conditions, the combustion efficiencies were 94.43–97.84% in boron and 95.14–98.24% in carbon.

After combustion, the combustion products were analyzed for CO_2, HNO_3, and H_3BO_3. The CO_2 content in gaseous products was determined gravimetrically (accuracy 3×10^4 g). The HNO_3 and H_3BO_3 contents were determined by alkaline titration: first HNO_3 form from nitrogen admixture in oxygen was titrated and then H_3BO_3 was titrated in the presence of mannitol. The titration results were used to calculate corrections for dissolution of H_3BO_3 and incomplete combustion of the compound studied.

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